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Interlaboratory test on polymers: determination of oxidation induction time and oxidation induction temperature by differential scanning calorimetry

Summary — The results of the oxidation induction time (*OIT*) tests indicate that the determination of *OIT* involves a high degree of uncertainty in respect of the measured data, particularly for low *OIT* values. This would seem to show that *OIT* measurements have an extremely critical significance for quality control purposes or lifetime predictions of polyolefin parts. Determining oxidation induction temperature (*OIT*^{*}) could therefore be a valuable alternative for less stabilized polyolefins (low *OIT* values) in particular. However, *OIT*^{*} measurement clearly indicates that the ability to distinguish between different samples decreases drastically as *OIT*^{*} data increase. Generally, the evaluated data can be used to estimate the results of in-house and external *OIT/OIT*^{*} measurements and their compatibility. This report should therefore support day-to-day work in analytical laboratories where oxidation induction values are measured by DSC.

Key words: interlaboratory test, polyethylene, oxidation induction time, oxidation induction temperature, statistical valuation of measurements, differential scanning calorimetry.

In this work the results of interlaboratory tests on oxidation induction time (*OIT*) and oxidation induction temperature (*OIT*^{*}), organized by EMPA, St. Gallen, are presented. EMPA St. Gallen organizes these tests on polymeric materials every two years. The participants are usually industrial laboratories and laboratories at institutes that test, research and develop polymeric materials. The presented interlaboratory test took place in 1998 and 2000. 14 participants in 1998 and 16 in 2000, mainly from industry and research institutes, measured *OIT* and *OIT*^{*} of four different grades of polyethylene by differential scanning calorimetry (DSC). The measured data were collected by EMPA and analyzed using a robust statistical method [1]. Repeatability and reproducibility data were of special interest.

INTERLABORATORY TESTING — GENERAL CHARACTERIZATION

Most important factors that produce deviations between individual measured results are:

a) the operator,

b) the equipment and the analytical instruments,
c) the calibration of the equipment and the instruments, and

d) the environmental effects during the test procedure, *i.e.* influence of temperature, humidity, light, pollution and so on.

The factors mentioned above are mathematically described by calculating the main characteristic interlaboratory results, the robust **standard deviation of repeatability** s_r [factors a), b), c) and d) are identical — **repeatability conditions**] and the robust **standard deviation of reproducibility** s_R [factors a), b), c) and d) are varied — **reproducibility conditions**]. The source and significance of these and other statistical terms used in interlaboratory tests are defined in Fig. 1.

Beside the robust standard deviations, the estimation of interlaboratory tests was also done using the corresponding limits. These values are defined as follows:

— **r = Repeatability limit** ($r = 2.8 \cdot s_r$): The value less than or equal to the absolute difference between two test results obtained under repeatability conditions may be expected to be within a probability of 95 %.

— **R = Reproducibility limit** ($R = 2.8 \cdot s_R$): The value less than or equal to the absolute difference between two test results obtained under reproducibility conditions may be expected to be within a probability of 95 %.

Finally, the ratio R/r is a measure of the quality of the measurement performance of the participants and the

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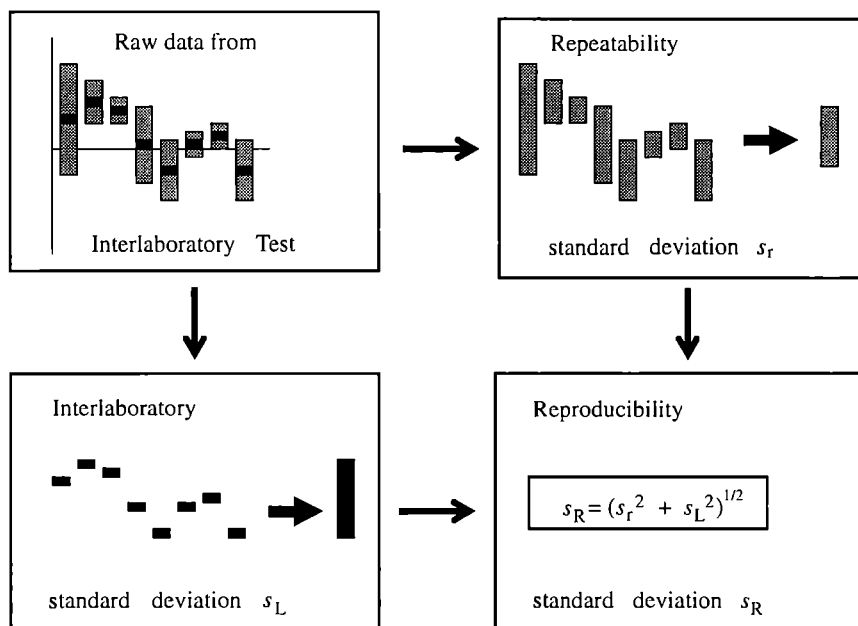


Fig. 1. Correlation between statistical terms (s_r , s_L and s_R)

interlaboratory test itself. For “good” and reliable interlaboratory tests the ratio should be within a range of about 2–3. If $R/r > 4$ it has to be assumed, that besides the above mentioned parameters a)–d) other parameters influence the results significantly. In this case the standard deviation of reproducibility (s_R) is almost entirely controlled by a major contribution outside the defined interlaboratory test conditions.

OXIDATION INDUCTION TIME AND OXIDATION INDUCTION TEMPERATURE

According to specific applications, plastic materials have to be stabilized to a greater or lesser extent against oxidation and environmental influences. A simple method to check the efficiency of the stabilizers or stabilizing systems used, is to determine the oxidation induction time or oxidation induction temperature of the molten material.

Especially for polyolefins, *OIT* and/or *OIT** measurements are well established for quality control purposes as a quick screening method to check the activity of the used stabilization system. The *OIT* measurement is most popular in this case. Many publications deal with this question [2]. The effects of different parameters on the precision of the results have been investigated in detail [3, 4] as well as the derivation of lifetime prediction for polyolefin tubes [5]. Influencing parameters which has to be mentioned in this connection are: sample weight, impurities (catalytical effect), sample surface and shape, flushing gas and flux, heating rate (*OIT**) and isothermal temperature (*OIT*). To minimize these effects the test programme was accurately prescribed for all the participating laboratories.

Principle of measurement

In this presentation, not only the well-established and popular *OIT* measurement is discussed, but the dynamic *OIT** measurement is introduced as well. Especially for *OIT* measurement a few standards are available (Table 1). The sequence of a standardized *OIT* measurement using DSC method according to EN 728 is outlined in Fig. 2. A sample of the polymer (approximately 15 mg) is placed in a clean aluminum pan. After posi-

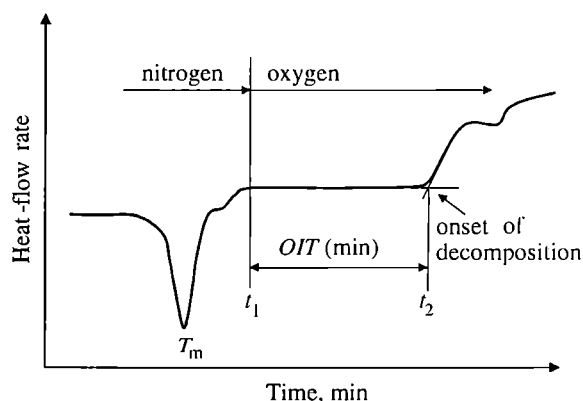


Fig. 2. Schematic diagram of the determination of *OIT* as the period between t_1 (onset of oxygen flow) and t_2 (onset of decomposition); explanation — see text

tioning the uncovered sample pan together with an empty reference pan in a calibrated DSC-oven, a nitrogen atmosphere is established in the measuring cell. Then, the sample and the reference are heated rapidly (at least = 20 K/min) to the temperature at which the *OIT* value is to be determined. When the required tempera-

ture is reached for the first time, an isothermal step of 3 minutes follows. After reaching this point (indicated as t_1 in Fig. 2) the atmosphere is switched to oxygen and the DSC-oven is held at the same temperature until an exothermic signal (oxidation) can be recognized. The onset of this oxidation signal corresponds to a time t_2 . The *OIT* value can now be determined as the time between t_1 and t_2 , described in Fig. 2.

Table 1. Actual Standards for *OIT* determination

Standard	Title
EN 728 (1997)	"Plastics piping and ducting systems — Polyolefin pipes and fittings — Determination of oxidation induction time"
ISO/CD 11357-6.3 (1999)	"Plastics — Differential Scanning Calorimetry (DSC) — Part 6: Oxidation Induction Time"
ASTM D 3895 (1995)	"Test Method for Oxidation Induction Time of Polyolefins by Differential Scanning Calorimetry"

Frequently however, the oxidation signal is less expressed than indicated in Fig. 2, making the determination of a clearly defined onset temperature difficult. Finding a suitable measuring temperature for the isothermal phase often causes further difficulties with *OIT* measurements. If the temperature is too low there is a substantial increase in the duration of the measurement and if the temperature is too high oxidation takes place immediately after the introduction of oxygen. The onset temperature of the decomposition signal (t_2) can no longer be determined.

Table 2. Comparison of the two oxidation induction measuring principles

Features	Measuring principle	
	<i>OIT</i>	<i>OIT</i> *
Standardized	yes	no (except in Finland)
Measuring method	static	dynamic
Preliminary tests	yes (evaluation of capable measuring temperature)	no
Gas change	yes (possible source of error)	no
Onset of oxidation signal	partially difficult to recognize and to analyze	mostly expressed very well and clear analyzable

The oxidation induction temperature (*OIT**) is evaluated in accordance with Fig. 3.

The sample is heated up continuously (*i.e.* 10 °C/min) under a pure oxygen (or air) gas flow. A change of gases

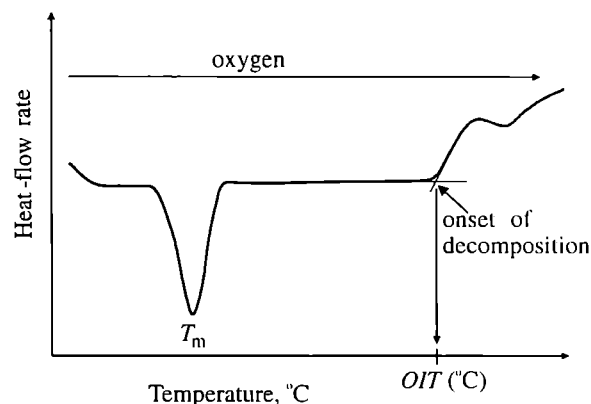


Fig. 3. Schematic diagram of the determination of *OIT** as the onset temperature of decomposition (explanation — see text)

at a defined time, as stated under *OIT* measurement, is not necessary. *OIT** is determined as that point in the thermogram, the onset of the decomposition signal results. *OIT** is usually more clearly expressed as the onset time t_2 in *OIT* measurements (t_2 is necessary for the determination of the *OIT* values).

Finally, to give an overview, the key points of both methods (determination of *OIT* versus *OIT**) are summarized in Table 2. Comparing the points in Table 2 it is obvious, that the *OIT** method needs less effort in setting up the measurements and in the majority of cases it gives clear defined onset points.

Samples

Four commercial grades of polyethylene with different levels of stabilization were chosen as test materials for the *OIT*/*OIT** test (see Table 3 for exact description of the materials). The materials were selected in such a way, that a board range of *OIT* values, suitable to industrial applications, was covered (*OIT* values between some minutes and more than one hour).

Table 3. Materials used in the interlaboratory test

Sample	Material	Producer	Type/visual characterization
Sample 1	PE-HD	BASF AG	Lupolen 4261 A/white powder
Sample 2	PE-LD	BASF AG	Lupolen 1852 H schw. 412/black granules
Sample 3	PE-HD	DOW Plastics	BG 10050/black granules
Sample 4	PE-HD	Hoechst	Hostalen CRP 100/black granules

Results of oxidation induction time (*OIT*)

The interlaboratory test data of the *OIT* values are summarized in Table 4. From the data in Table 4, it is possible to establish that the repeatability and reproduci-

bility of the *OIT* values depend on the order of magnitude of the median values of the samples. The lower the *OIT* median values, the greater the relative values (s_r relative, s_R relative) of the standard deviations. This correlation becomes clearer if the data of the actual ring test are compared with data from other interlaboratory tests (see Table 5).

Table 4. *OIT* median values, standard deviations (s_r , s_R), relative standard deviations (s_r relative, s_R relative), repeatability and reproducibility limits (r , R) of the four PE ring test materials

Value, unit	Sample 1 (PE-HD)	Sample 2 (PE-LD)	Sample 3 (PE-HD)	Sample 4 (PE-HD)
<i>OIT</i> median value, min	3.4	18.9	36.9	62.4
s_r , min	0.6	1.2	2.1	1.7
s_r relative ^{a)} , %	17.8	6.1	5.8	2.7
s_R , min	2.1	2.0	6.5	9.5
s_R relative ^{a)} , %	62.1	10.8	17.6	15.3
r , min	1.7	3.2	5.9	4.8
R , min	6.0	5.7	18.2	26.6
R/r	3.5	1.8	3.1	5.5

^{a)} s_r, s_R relative (%) = (s_r or s_R · 100 %)/median value.

Table 5. Comparison of s_r relative and s_R relative^{a)} of *OIT* data from own (EMPA) and foreign interlaboratory tests (described in the mentioned standards)

Data from own and foreign interlaboratory tests	Material	Number of participants	Interlaboratory test key data		
			<i>OIT</i> median value min	s_r relative %	s_R relative %
EMPA 1998 ^{b)}	PE-HD	14	3.4	15.4	64.7
ÖKI 2000 ^{c)}	PE-HD	13	3.7	33.7	62.2
ÖKI 2000 ^{c)}	PE-HD	12	9.3	11.8	64.1
EMPA 1998 ^{b)}	PE-LD	14	18.9	6.9	11.1
ASTM D 3895 ^{d)}	PE-LD	11	23.4	13.2	20.1
ISO/CD 11357-6 ^{e)}	PE-LD	— ^{e)}	24.0	11.7	17.9
EMPA 2000 ^{b)}	PE-HD	16	36.9	5.8	17.6
EMPA 2000 ^{b)}	PE-HD	16	62.4	2.7	15.3
ASTM D 3895 ^{d)}	PE-LD	11	79.9	11.4	18.9
ISO/CD 11357-6 ^{e)}	PE-LD	— ^{e)}	83.4	11.0	20.9
ASTM D 3895 ^{d)}	PE-LLD	11	119	6.6	14.0
ISO/CD 11357-6 ^{e)}	PE-LLD	— ^{e)}	120	6.5	12.2
ISO/CD 11357-6 ^{e)}	PE-HD	— ^{e)}	163	5.1	13.3
ASTM D 3895 ^{d)}	PE-HD	11	166	4.9	14.5

^{a)} s_r and s_R relative — see Table 4.

^{b)} Interlaboratory test performed by EMPA in 1998 and 2000; evaluation of data with robust statistics.

^{c)} Interlaboratory test performed by the Austrian Plastics Institute; evaluation of data according ISO 5725-2 with consideration of outliers.

^{d)} Interlaboratory test performed by ASTM in 1991; evaluation of data with ASTM E 691.

^{e)} Not specified regarding evaluation method and number of participants.

From the data in Table 5, is it possible to see, as a tendency, what influence the *OIT* median values exert on the s_r and s_R results. The lower the *OIT* value, the greater the relative standard deviation becomes. This could be

seen for the relative reproducibility standard deviation (s_R relative) in particular. Even a border line within the range of 10 to 20 min seems to be present, below which the s_R values rise significantly (relative reproducibility standard deviations greater than 60 %!). Evaluations of *OIT* values of the samples with very low stabilizer amount (*OIT* lower than 15 min) must therefore be regarded as critical. One possibility to improve the precision of *OIT* in that case could be to lower the isothermal temperature in order to increase t_2 to a time region above 20 minutes.

Results of oxidation induction temperature (*OIT*^{*})

The key data of the interlaboratory test obtained from the evaluation of the *OIT*^{*} values are summarized in Table 6. The standard deviations of the temperature values in Table 6 seem to be reasonable because they have a similar order of magnitude as those found in other interlaboratory tests, where temperature were evaluated by means of DSC measurements [6, 7]. In the case of temperature measurements, it is quite clear that calculated relative values (s_r relative and s_R relative) strongly depend on the temperature scale used. For instance, if absolute temperatures (Kelvin scale) are used in our interlaboratory tests, the relative standard deviation would become smaller. Another proposal could be to define the melting point of every material as the zero point of the respective *OIT*^{*} measurement. In this case the relative

Table 6. *OIT*^{*} median values, standard deviations (s_r , s_R), relative standard deviations (s_r relative, s_R relative), repeatability and reproducibility limits (r , R) of the four PE interlaboratory test materials

Value, unit	Sample 1 (PE-HD)	Sample 2 (PE-LD)	Sample 3 (PE-HD)	Sample 4 (PE-HD)
<i>OIT</i> [*] median value, °C	217	242	248	254
s_r (repeatability), °C	2.4	0.7	0.9	1.5
s_r relative ^{a)} , %	1.1	0.3	0.4	0.6
s_R (reproducibility), °C	4.0	2.2	2.8	4.1
s_R relative ^{a)} , %	1.8	0.9	1.2	1.6
r , °C	6.7	1.9	2.5	4.2
R , °C	11.1	6.1	7.8	11.5
R/r	1.7	3.2	3.1	2.7

^{a)} s_r and s_R relative — see Table 4.

standard deviations would increase substantially. In our interlaboratory test, we decided to use temperatures corresponding to the centigrade scale, because it is quite common in DSC measurements. Therefore, all further discussions and comparisons of relative temperature data refer to °C.

Comparison of *OIT* and *OIT*^{*} data

Table 7 summarizes the median values, standard deviations (s_r , s_R) and relative standard deviations (s_r rela-

Table 7. *OIT* and *OIT*^{*} median values, standard deviations (s_r , s_R) and relative standard deviations (s_r relative^{*)}, s_R relative^{*)}) of the four PE interlaboratory test samples

Sample	Method	Median values	s_r	s_r relative ^{*)} , %	s_R	s_R relative ^{*)} , %
Sample 1 (PE-HD)	<i>OIT</i>	3.0 min	0.5 min	15.4	2.2 min	64.8
	<i>OIT</i> [*]	217 °C	2.4 °C	1.1	4.0 °C	1.8
Sample 2 (PE-LD)	<i>OIT</i>	18.9 min	1.2 min	6.2	2.1 min	11.0
	<i>OIT</i> [*]	242 °C	0.7 °C	0.3	2.2 °C	0.9
Sample 3 (PE-HD)	<i>OIT</i>	36.9 min	2.1 min	5.8	6.5 min	17.6
	<i>OIT</i> [*]	248 °C	0.9 °C	0.4	2.8 °C	1.1
Sample 4 (PE-HD)	<i>OIT</i>	62.4 min	1.7 min	2.7	9.5 min	15.3
	<i>OIT</i> [*]	254 °C	1.5 °C	0.6	4.1 °C	1.6

^{*)} s_r and s_R relative — see Table 4.

tive, s_R relative) of the four PE samples and two oxidation induction methods. By comparing s_r relative and s_R relative values of *OIT* and *OIT*^{*} data it can be seen that the dynamic measurement (*OIT*^{*}) is related to significantly smaller relative standard deviations than the static *OIT* method. It is true for both cases, *i.e.* the repeatability standard deviation and reproducibility standard deviation. This could lead to the interpretation, that *OIT*^{*} measurements are always more reproducible than *OIT* tests and should be preferred. Additionally, also the set up of *OIT*^{*} measurements is even easier.

However if one compares the absolute values, then it is noticeable that for *OIT*^{*} measurements the differentiability between individual samples decreases significantly with rising temperature. This correlation is shown clearly in Fig. 4. The four PE interlaboratory tests samples are plotted here as *OIT*/*OIT*^{*} diagram with the me-

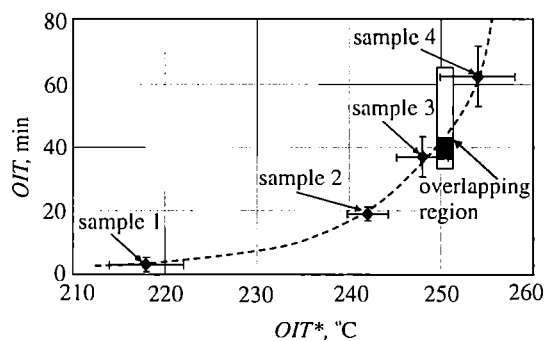


Fig. 4. X, Y-pair of *OIT*/*OIT*^{*} values (symbol ♦) of the four PE ring test samples with the corresponding reproducibility standard deviations (s_R) as uncertainty bars (further explanation — see text)

dian values as x , y values and the reproducibility standard deviations (s_R) as uncertainty bars. It can be clearly seen that due to the exponential character of the oxidative decomposition of plastics with respect to temperature (dotted line in Fig. 4), *OIT*^{*} values above approx. 240 °C lead to a cumulative accumulation of the measured *OIT*^{*} values. This finally leads to an overlap of the error bars concerning abscissa (overlapping region in

Fig. 4). Thus, the differentiation between samples no longer exists in the case of the *OIT*^{*} values despite very small relative standard deviations (*e.g.* sample 3 and sample 4 may give the same *OIT*^{*} result although they contain a different amount of oxidation stabilizers). In contrast to that, it is possible to distinguish the samples by way of the *OIT* values (ordinate axis) despite high relative standard deviations.

Finally the R/r -ratio for both measurements (*OIT* and *OIT*^{*}) for almost all samples is close to the required and expected range of 2–3 (single values of R/r tabulated in Table 4 and Table 6). The measuring performance of all participants seems to be rather good and the reproducibility limit R is not influenced by unknown and uncontrollable factors.

CONCLUSIONS

The present report indicates what repeatability and reproducibility standard deviations and what corresponding limits must be taken into account when oxidation induction time or temperature measurements are performed using DSC method. At a glance, the report should therefore provide support for day-to-day work in analytical laboratories where *OIT* data are measured.

The data from this *OIT* interlaboratory test demonstrate that the determination of the oxidation induction time shows a substantial variation in the measured values, particularly for very low *OIT* values. Here, only a reduction of the temperature of the isothermal phase ($T < 210$ °C) or a reduction of the oxygen content in the measuring chamber could increase the differentiability of similar samples. The high values of repeatability and reproducibility standard deviations also show that the significance of *OIT* measurements, *e.g.* with regard to quality control or lifetime predictions of polyolefin parts, is to be viewed rather critically.

Particularly for very low *OIT* values (polyolefins with low stabilizers concentration) the dynamic procedure of the determination of the oxidation induction temperature seems to be a good alternative. But, the *OIT*^{*} data also show clearly that differentiation between individual samples decreases rapidly when *OIT*^{*} values increase.

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